Reply to cond-mat/0211660: Comments on "A model for fatigue in ferroelectric perovskite thin films" published in Appl. Phys. Lett, 76, 1060 (2000); addendum, ibid. p.3655

Matthew Dawber and James F. Scott

Centre for Ferroics, Dept of Earth Sciences, Downing St, Cambridge, CB2 3EQ, UK.
Email: mdaw00@esc.cam.ac.uk, jsco99@esc.cam.ac.uk

Although the appropriate forum for discussion of published papers should be the journal itself through the properly refereed process where we are given an opportunity to have a reply published simultaneously with the comments, Taganstev has chosen instead to attack our paper through this unrefereed forum. In this context it is worth noting that the comments that Tagantsev has made were in fact submitted to Applied Physics Letters more than two years ago. At that time we wrote a reply to these comments. The decision of the referee at that time was that Tagantsev's comment was wrong and should not be published. Although we do not feel this is the appropriate forum for this discussion, Tagantsev has chosen to resume this debate in the unrefereed public forum of cond-mat and so we feel the need to defend ourselves against the 8 points he has raised.

Our model was a first attempt to produce a quantitative analytic model for fatigue based on earlier work by Yoo and Desu, and as such requires further testing and development. We note that our model has already been extended and applied successfully by Wang et al. (Physica Status Solidi A, **191** 482 (2002)). Tagantsev's "model" for fatigue is untestable (falsifiable).We would encourage feedback from other authors who have attempted to apply our model, and are always happy to discuss our work. Please contact us directly on the above email addresses if you have any concerns about the publications mentioned here.

1. Taganstsev objects to our use of the Onsager expression for the local field at an oxygen vacancy, preferring instead an expression that is linear in the dielectric constant. One wonders what might happen when a ferroelectric goes through its phase transition and the dielectric constant (and hence local field, if one uses Taganstev's expression) diverges. The Tagantsev model of ferroelectric detonation in which internal fields diverge as a ferroelectric material

is field cooled through its transition temperature does not seem to have been experimentally observed. Perhaps one should look beyond undergraduate textbooks such as Kittel's. A more detailed calculation of the effective charge on an oxygen vacancy has been recently undertaken by Prof. S.A. Prosandeev (cond-mat/0209019) in which he found that our result was much more appropriate than Taganstev's.

2. Taganstev claims that our equation is quite different from that of O'Dwyer. Simple inspection of the two equations show that this is not true. In the high field limit sinh(x)=exp(x), and as our local field is only 1.5 times the applied field Taganstev's claim that use of this field changes the result by "orders of magnitude" is clearly unfounded.

3.Tagantsev's point on equation 10 is taken. The reason that there appears to be a change in the oxygen vacancy concentration at the interface in the absence of an applied field is that we have used the high field limit of the sinh(x) term in the diffusion equation ie. (exp(x)). This means that our equations are not appropriate for low fields, but it should be noted that during polarisation switching high fields are applied. The reason for the use of the exponential limit of the sinh term was so as to simplify the derivation that followed.

4.We consider that the approximations we have taken are appropriate for the situation. The applied field in our model is very high because the applied potential falls across a quite narrow depletion region in the ferroelectric. Therefore in our opinion the space charge field is not significant compared to the applied field.

Tagantsev is correct that one would expect to see an increase in concentration of charge at the electrodes in non-ferroelectric back-to-back Schottky diodes, however his claim that this has never been observed is false. This has been observed for at least twenty years in zinc oxide varistors. (e.g. Hayashi et al., J. Appl. Phys. **58** 5754 (1982)) Thus his argument helps prove our model - as confirmed by Hayashi.

5. The activation energy of electrons was used to calculate the number of oxygen vacancies that would be charged, not the concentration of oxygen vacancies. The activation energy of 0.7 eV in fact corresponds to the trapping energy of Ti^{3+} which is known to be associated with oxygen vacancies. We originally considered that the important activation energy originated from the charge state of the oxygen vacancy. However following our new ideas on oxygen vacancy ordering we believe that the entropy term is more important than originally anticipated. We would refer readers to further references on this subject for more details. (J.F. Scott and M. Dawber, Appl. Phys. Lett. **76** 3801 (2000), M. Dawber and J. F. Scott, Integr. Ferroelectr. **32** 951 (2001) J. F. Scott, Ferroelectric Memories (Springer, Heidelberg, 2000), pp. 134)

6. Ref. 6 of Tagantsev's paper was originally cited by us because it gave a reasonable number for the depletion width, which we used in our calculations. In the years since we published our paper we have re-examined the data of reference 6. We are no longer convinced that the current observed in this paper is in fact Fowler-Nordheim tunneling. We do not wish to further criticize this paper in this unrefereed forum, but any interested reader should attempt to fit

the data of ref 6 to a Schottky plot to see the origin of our concerns. Readers can contact us directly for a more detailed explanation of these concerns which are partly based on our own unpublished results. We also have concerns about the effective masses used in Tagantsev's analysis and the lack of specification of carrier type (electron/hole). [Their m* = 1.4 m_e (Bull Am Phys Soc, Seattle, March 2001) value disagrees by x4 with the known electron band mass, and in undoped PZT films the carriers are NOT holes.] We have previously discussed these problems elsewhere (J.F. Scott, Integr. Ferroelectr. **42** 1 (2002).

7. In our original paper the figure was incorrectly labelled due to technical error in journal production. Our addendum clearly acknowledges this error. We apologize for any confusion caused by this error. The prediction of the equations in both papers is in line with the data of Mihara.

8. Our model does predict a frequency dependence for fatigue. This has been seen in other papers than that of Colla et al., where it is true that the use of different waveforms complicates interpretation. Examples of such papers include, Lee et al, Appl. Phys. Lett. **79** 821 (2001) ; Zhang et al., Ferroelectrics, **259** 109 (2001).